THE POTENTIAL OF C^{13} NMR IN COAL RESEARCH

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SUMMARY

Current carbon-13 nuclear magnetic resonance (C^{13} NMR) studies of coal, coal derivatives, and related materials are presented and discussed. Broadline and pulsed NMR techniques have been applied to a few solid materials isotopically enriched in carbon-13, while high-resolution NMR studies of a wide variety of pure compounds and several coal derivatives have been carried out. The former techniques are used to derive spectral second moments and nuclear magnetic relaxation times. High-resolution C^{13} NMR is potentially a powerful tool for the direct quantitative determination of the aromaticity (f_a) of soluble products from coal. Values of f_a for light oils from coal and lignite and for a carbon disulfide extract of coal have been estimated from their C^{13} NMR spectra.

INTRODUCTION

Since the first published report of successful NMR measurements of the hydrogen distribution in a coal derivative[1] and the first determination of a high-resolution spectrum of a coal extract[2], proton magnetic resonance spectrometry has been used by many authors[3] to aid in the elucidation of the structure of coal. Brown and Ladner[4] developed a method for applying the hydrogen distribution data to the analysis of carbon structure, with particular emphasis on estimating three important structural parameters: f_a, the aromaticity; σ, the degree of aromatic substitution; and H_{aru}/C_{ar}, an indication of the size of the condensed aromatic ring system. C^{13} NMR offers a method by which f_a can be measured directly and realistic limiting values can be placed on the latter two parameters.

Broadline NMR, first observed for the protons in coal by Newman, Pratt, and Richards[5], is a means of determining second moments and may for very simple molecules give information on hydrogen-hydrogen distances. Values of various parameters for the mean structural units in coals have been estimated from experimentally determined second moments.[3] C^{13} NMR has been detected in natural abundance for only a few solid substances; the principal investigators being Lauterbur[6] and Davis and Kurland[7]. Observation of the C^{13} resonance in graphite has been reported by Abragam[8] using the method of Overhauser dynamic polarization. An attempt to find the C^{13} resonance in synthetic diamond proved unsuccessful[9]. Solid state C^{13} NMR studies of C^{13} enriched materials may give information on carbon-carbon or carbon-hydrogen bond distances[10].

No measurements of relaxation times for nuclei in coal have been reported in the literature to date and C^{13} nuclear relaxation times have been reported for only two substances containing naturally occurring carbon-13[11]. Preliminary measurements of proton relaxation times in a bituminous coal and C^{13} relaxation times in a few isotopically enriched materials were carried out under Bureau supervision during the course of this investigation.

EXPERIMENTAL

The high-resolution C^{13} NMR spectra obtained during the course of this investigation were of two types. Rapid passage dispersion mode C^{13} spectra were obtained using a Varian Associates V-4300C high-resolution NMR spectrometer operating at 15.085 MHz. These spectra exhibit asymmetric peaks, do not have a continuous baseline, and peak shapes and intensities are dependent upon the direction of magnetic field sweep. Thus, spectra are presented in pairs with the spectrum obtained while sweeping the applied magnetic field from low to high values being at the top of each figure. Quantitative estimates of f_a were determined by the method of Friedel and Retcofsky[12]. Time-averaged absorption mode C^{13} spectra were kindly provided by E. G. Cummins of Perkin-Elmer, Ltd., and were obtained using an R-10 spectrometer. Values of f_a were determined directly from electronic integration of the spectra.

Broadline C^{13} NMR spectra were also obtained on the Varian instrument mentioned above. The modulation and detection systems used for the broadline studies were components of a Varian V-4500 electron paramagnetic resonance spectrometer.

C^{13} magnetic relaxation times were measured from oscillographic recordings of free induction decay curves (for T_2) and of the NMR signal amplitude following 180°-90° pulse sequences (for T_1). This work was generously performed for us by NMR Specialties, Inc., using their PS-60-A pulsed spectrometer system.

RESULTS AND DISCUSSION

High-Resolution Studies

Rapid passage dispersion mode spectra of neutral oils from coal and lignite are shown in figures 1 and 2 respectively. The signal-to-noise ratio, although not high and certainly not an important limiting factor in accurate determinations of f_a, is remarkably good considering the low natural abundance of C^{13}, and the complexity of the coal derivatives. The higher aromaticity of the oil from high-temperature cracking of the coal carbonization product is readily apparent from the spectra. Aromaticities for three neutral oils were estimated using the calibration procedures reported previously. The results are given in the table below and compared with f_a's estimated from proton NMR data by the Brown and Ladner[4] method. Spectra of a CS$_2$ extract of coal (representing 3% to 5% of the whole coal) are shown in figure 3. The signal-to-noise ratio here is considerably worse due to the presence of a large amount of the CS_2 solvent. The f_a value determined from C^{13} NMR is 0.6.

Aromaticities of Neutral Oils

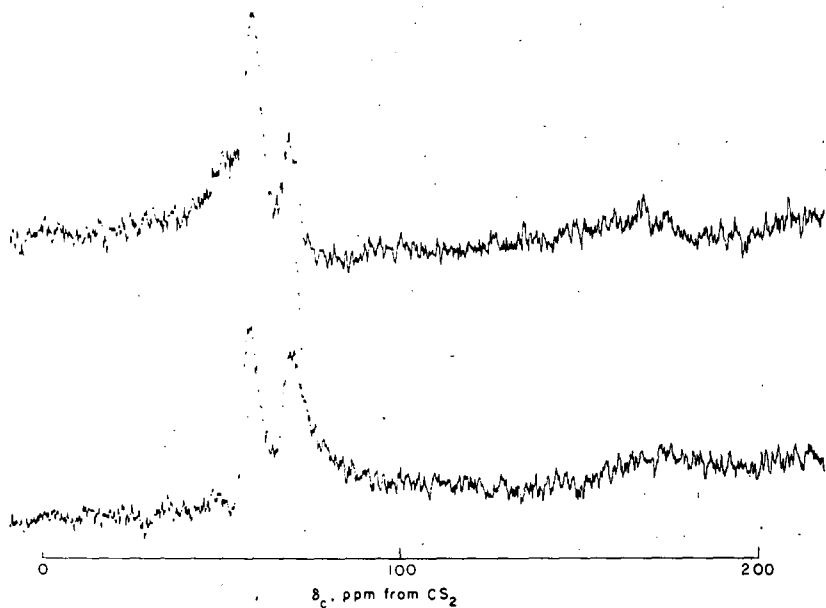| Source	C/H	f_a	
		H^1	C^{13}
800° C cracking of a high-temperature coal carbonization product	1.05	0.83	0.78
700° C cracking of a low-temperature coal carbonization product	0.86	0.68	0.70
Distillation of a lignite carbonization product	0.64	0.38	0.39

δ_c. ppm from CS_2

Figure 1. C^{13} magnetic resonance spectra of neutral oil from 800°C cracking of condensed tar from High Splint Coal.

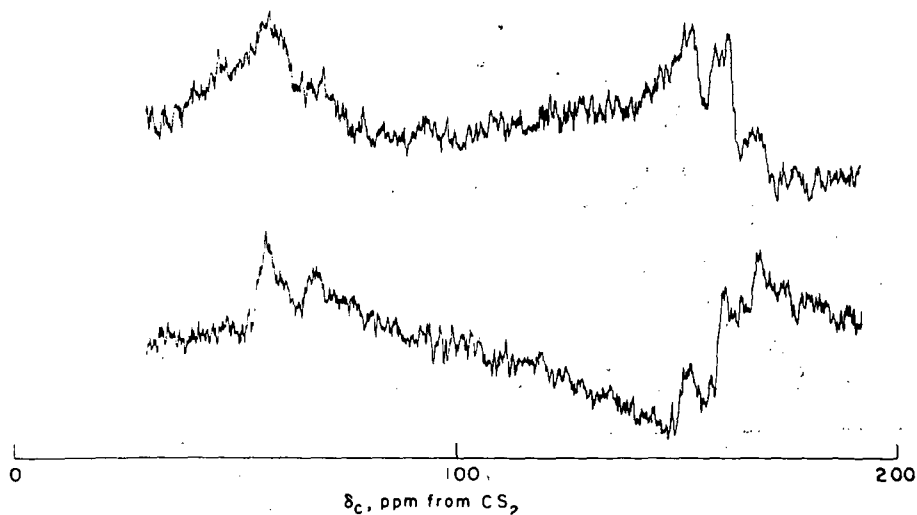

δ_c, ppm from CS_2

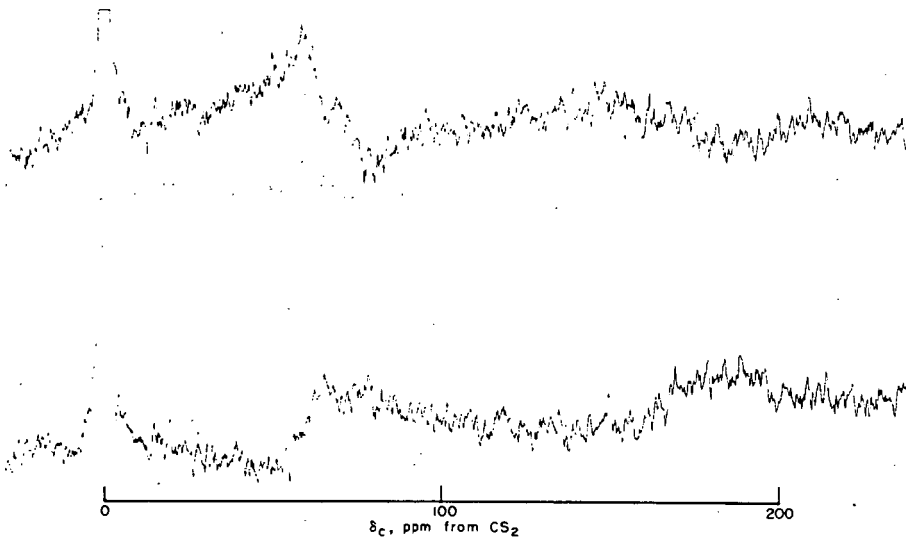Figure 2. C^{13} magnetic resonance spectra of neutral oil from distillation of Sandow Lignite Tar.

Figure 3. C^{13} magnetic resonance spectra of carbon disulfide extract of Pittsburgh Seam Vitrain.
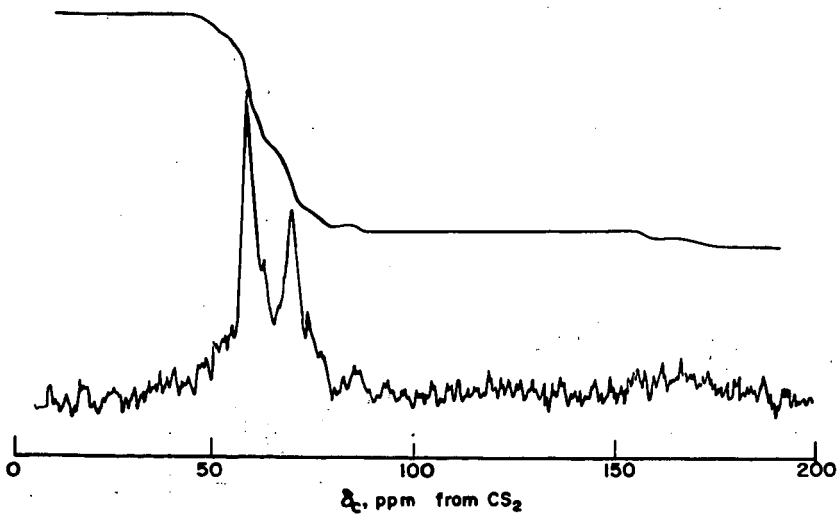

Figure 4. Absorption mode C^{13} magnetic resonance spectrum of coal tar.

The disadvantages in trying to obtain quantitative values of f_a from rapid passage dispersion mode C^{13} spectra are obvious from figures 1 and 2 and have been indicated in the foregoing discussion. Nevertheless it must be remembered that this is the first direct method for determining this heretofore very elusive structural parameter. With the advent of the time-averaging computer and its successful application in NMR experiments, the time is now here that highly precise and reasonably accurate f_a values can be obtained from absorption mode C^{13} NMR spectra. That is, spectra can be obtained under conditions similar to those used in proton NMR. Such a spectrum obtained from nearly 1,000 scans of the C^{13} spectral region is shown in figure 4 for the CS_2-soluble material of coal tar. The f_a value can be gotten directly from the integral reproduced along with the spectrum. The potential of this technique in coal structure research is an exciting one and will be pursued in our laboratory.

Broadline NMR

The C^{13} NMR spectrum of an isotopically enriched amorphous carbon produced by the 1000° C reduction of $C^{13}O_2$ is shown in figure 5. The spectrum shown is handdrawn using 6 actual spectra as guides. Isotopic enrichment is around 55 percent. The peak to peak linewidth is 5.2 gauss and the second moment was measured to be 6.0 guass[2]. The spectral linewidth of the carbon can be compared to that found for barium carbonate (around 1.0 gauss) in which dipole-dipole interactions are essentially negligible and the width is determined primarily by the chemical shift anisotropy[6] of the carbonate anion.

Pulsed NMR

The C^{13} enriched carbon was also examined by pulsed NMR techniques. Room temperature measurements of the spin-lattice relaxation time (T_1) and the spin-spin relaxation time (T_2) yielded the values 360 milliseconds and 80 microseconds respectively. The free precession decay curve is shown in figure 6. One important conclusion that can be made from these measurements is that the transmitter power level used for obtaining the broadline NMR spectrum was low enough to avoid saturation. Thus true line shapes are observed. T_1 and T_2 were found to be 27 seconds and 13 seconds respectively for the carbonyl carbon in 55% C^{13} enriched liquid acetic acid. In contrast the proton relaxation times in an 84% carbon coal are 50 microseconds (T_1) and 9 microseconds (T_2).

CONCLUSIONS

The carbon-13 NMR results described here illustrate the first application of the technique to coal derivatives. The potential of the techniques described is nearly unlimited and possibly much more information than that described here will be obtained. For example, C^{13} has been shown to be a very useful tool for the characterization of carbonyl groups. Such groups are thought to be present in coal. The most recent experimental techniques involve the use of time averaging computers, instruments which are at this time beginning to appear on the work bench of many industrial, government, and academic research laboratories. The main disadvantage to C^{13} NMR spectroscopy is the long times involved in the accumulation of spectral data. Thus, although it may not become as widely applied as NMR of other nuclei such as H^1 and F^{19}, the information obtained from C^{13} NMR may be much, much more important.
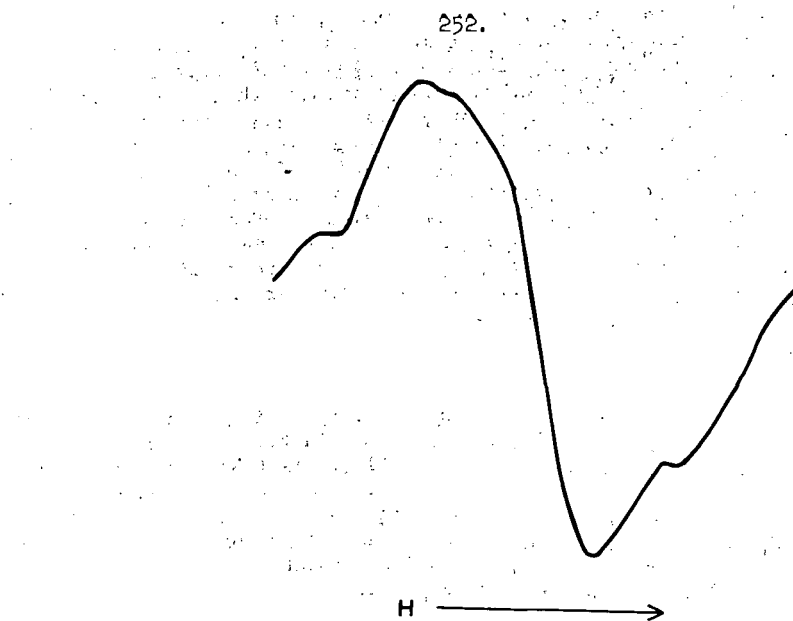
H ⟶

Figure 5. C^{13} magnetic resonance spectrum of amorphous carbon.
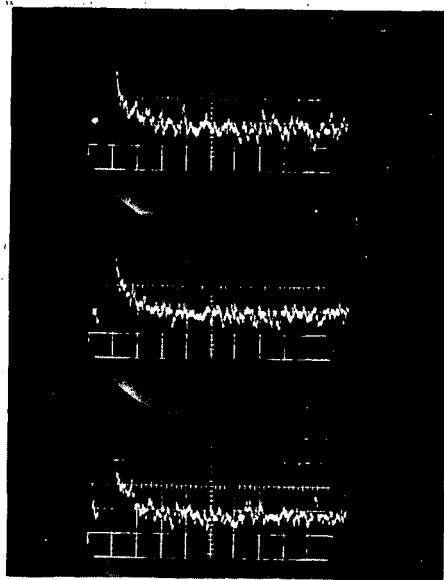(55% enriched in carbon-13)

Figure 6. Free induction decay curves for amorphous carbon.

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